PERCHLOROETHYLENE EXTRACTION OF SULFUR AND SULFUR COMPOUNDS FROM COAL

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ABSTRACT

Perchloroethylene (PCE) is an excellent solvent for extracting elemental sulfur ($S°$) from bituminous coal. The same amount of $S°$ is extracted within one hour at reflux (120°C) or 72 hours at 27°C. Extractions at 120°C also remove 1-2 weight % organic material within 30 minutes. Additional heating increases the amount of organic material extracted but decreases the concentration of $S°$ in solution due to reactions between sulfur and coal. The elemental sulfur content of ten different mid-western coal samples varies with the sulfatic sulfur content, consistent with the view that both elemental sulfur and sulfate in coal come from weathering of pyrite. The nature of the organosulfur compounds extracted by PCE and by THF has been studied by Sulfur Sensitive Gas Chromatography and GC/MS as described in an accompanying paper by K. Vorres.

INTRODUCTION

Previous studies have shown that hot perchloroethylene (PCE) extracts significant quantities of elemental sulfur ($S°$) from several mid-western coals. Narayan reported that 1.6% $S°$ by weight was recovered from an Indiana refuse coal and speculated that organic sulfur in coal may in fact exist as insoluble polysulfides which are converted to soluble orthorhombic sulfur (S_8) by hot PCE.[1] S. Lee and H. Leehe have reported that ASTM organic sulfur is reduced in the PCE-insoluble product coals after PCE extraction and they have qualitatively identified $S°$ in the extracts.[2][3] However, other studies have shown that little or no $S°$ is found in most US coals using other methods.[4][5][6] Removal of significant amounts of organic sulfur from coal by simple solvent extraction would be an important contribution to pre-combustion desulfurization.

We have shown that only small amounts of $S°$ are extracted by PCE from Illinois coals and that only weathered coals contain extractable $S°$.[7] For at least one coal, pyrite oxidation was shown to be the source of the $S°$ extracted.[8] IBC-107 is an Illinois No. 6 coal in which the forms of sulfur have characteristic stable sulfur isotope ratios (SSIR, ^{34}). In this coal, the SSIR for the organic sulfur is 1.9°/oo, for sulfatic sulfur 13.2°/oo and for pyritic sulfur 24.0°/oo. The elemental sulfur isolated from this coal had an SSIR value of 19.8°/oo, showing that it was derived from the pyritic rather than the organic fraction of the sulfur in this coal.[8]

Temperature and contact time were found to be important variables for both the reduction of organic sulfur and yield of $S°$ by PCE extraction.[1-3][7] Long term heating of weathered coal with PCE reduces the yield of $S°$.[9] We now report on the effect of temperature on the extraction of $S°$ from coals and on the isolation and chromatographic fractionation of organic compounds extracted by PCE. Because early reports on PCE extraction emphasized the isolation of only elemental sulfur, it is important to note that organosulfur compounds are also present in PCE extracts. The identification of organosulfur compounds in these extracts is discussed in the accompanying paper by Vorres.[10]

EXPERIMENTAL PROCEDURES

Coal samples use were Illinois Basin Coal Sample Program (Illinois State Geological Survey - ISGS) IBC-101, -201, -501, and -701; Argonne Premium Coal Sample Program coal No. 3 plus an oxidized version of this coal; an Ohio 5/6 coal from Horizon Coal Co. (C.J. Kulik) and an Indiana Refuse coal (R. Narayan). Unless otherwise noted, all coal samples and solid products were dried to constant weight at 0.1 Torr., 100°C in an Abderhalden apparatus before use or before final weights were determined. Samples were supplied as either -60 or -100 mesh material and were not further reduced in size. Ultimate analyses and ASTM Forms of Sulfur analyses of the actual samples of all feed coals and solid products were performed under the supervision of Dr. Chusak Chaven at the ISGS.

HPLC grade PCE (Aldrich) was fractionally distilled before use to remove traces of a UV-active material which interfered with the UV detector used in the HPLC determination of elemental sulfur. Elemental sulfur for preparation of analytical standards and reactions with coal was sublimed immediately before use to remove traces of amorphous sulfur which did not completely dissolve in PCE.

The Soxhlet extraction method developed for PCE is slightly modified from that reported earlier.[11] A thermometer or thermocouple probe was arranged to measure the temperature inside the extraction thimble in the upper one third of the coal mass. An electric heating tape (Brisket) was wrapped around the glass barrel holding the thimble and the PCE inside was maintained at a slow boil (120°C) during the extraction. Under these conditions, any constriction in the siphon tube of the apparatus interrupted smooth cycling of hot solvent. Solvent was added to the apparatus and brought to temperature and the coal sample added to the solvent in the thimble. At the end of the extraction, the contents of the thimble were vacuum filtered on a 0.45 um PTFE membrane filter. In batch extraction experiments, a weighed sample of dry coal was quickly added to a measured volume of well-stirred PCE in a round-bottom flask maintained at a known temperature with an electrically heated oil bath. Product coal was recovered by hot filtration in which the filter funnel and filter paper were heated by boiling PCE vapors from the receiver flask. A thermometer was suspended such that the temperature of the slurry in the filter was measured and maintained above 118°C.

Product coals were recovered by washing with hot 80% methanol/water, filtration and vacuum drying or by steam distilling PCE away from the coal residue. Aliquots of the solvent extracts were analyzed for elemental sulfur by HPLC after passage through a dry-packed Florisil chromatography column (1cm x 30cm) to remove organic compounds which interfere with the analysis. Column flow was adjusted to 1 drop per second and sample eluted with additional pure PCE. The second milliliter to elute from the column was collected for HPLC analysis on a 4.6 x 250 mm C_{18} reversed phase HPLC column using a mobile phase of 95% methanol/water at 1.5 mL/minute with UV detection at 290 nm. The method was calibrated with standard solutions of sublimed S° in distilled PCE. The calibration samples were also passed through a Florisil clean-up column.

PCE and THF extracts were fractionated for GC/MS studies by published methods.[12][13] Solvent-free extracts were chromatographed on alumina using hexane, benzene, chloroform and THF/10% ethanol in sequence. PAC fractions (benzene) were re-chromatographed on silica gel impregnated with $PdCl_2$.

RESULTS AND DISCUSSION

Yields of elemental sulfur extracted are given in Table 1 along with ASTM Forms of Sulfur analyses. A less complete version of this data set has been presented elsewhere.[7][9] Linear least-squares correlations between weight percent elemental sulfur extracted by PCE and weight percent sulfatic sulfur (ASTM) are

shown below the data. Since S° is both produced and consumed during pyrite
oxidation, the numerical value of the relationship is probably not a simple ratio
of reaction rate constants. The significance of the data is that S° is only
found in weathered coals, and then in amounts proportional to sulfatic sulfur
which is widely conceded to arise from pyrite oxidation. These results, taken
with the stable sulfur isotope ratio study,(8) make a strong case for pyrite
oxidation as the only source of S° necessary to explain PCE extractions.

The reduction in ASTM organic sulfur in the product coals (PCE-insoluble
residues) ranged from 2 to 24% by weight. Total sulfur material balances
(product coal, PCE extract and wash solvent, if any) ranged from 87 to 102%, with
most values from 92 to 96% by weight, Table 2. To date, only coal 0560 has given
an organic sulfur reduction above 11%. Because of the many errors in ASTM
organic sulfur values, it is important to determine how all of the sulfur in the
feed coal is distributed among the product fractions and not just report an
apparent loss of sulfur from one fraction.

Our preliminary studies(7) and others(2)(3) have shown that extractions at 90-
110°C recover less S° than those in which the temperature is carefully maintained
at 120°C, the boiling point of PCE. Additional heating at 90 - 115°C decreases
rather than increases the yield of S° extracted. The studies summarized in
Figures 1 and 2 show this behavior to derive from two competing processes - rapid
solution of S° by processes proceeding even at 27°C, and retrograde reactions
between sulfur and coal which occur only at the higher temperature.

Figure 1 shows that the same yield of S° is obtained from IBC-101 coal in a batch
extraction after 72 hours at 27°C as was obtained under optimum Soxhlet
extraction conditions, 3 hours at 120°C. At 120°C, the maximum yields in batch
extractions occur at one half hour. Figure 2 shows the decrease in concentration
of S° remaining in solution when approximately 12 g of APCSP No. 3 coal or a
heavily oxidized fraction of that coal (E0935, Table 1) was heated with 1.7
millimoles of elemental sulfur in 150 mL of PCE at 120°C for 816 hours under
nitrogen. A control experiment minus the coal did not lose appreciable amounts
of sulfur during that time. The initial increase in S° concentration for E0935
is due to solution of the S° originally present. A plot of $\ln[S°/S°_{int}]$ vs time
for the premium coal was linear through four half lives and gave an apparent
first-order rate constant of 9.7×10^{-7} sec.$^{-1}$ for the disappearance of sulfur.

Conditions which maximize the yield of S° do not maximize the yield of organic
compounds also extractable from coal. PCE extracts 1-2% by weight organic
material from coals. The solvent-free extracts have elemental compositions
similar to toluene extracts of the same coals,(11) as expected for a non-polar,
non-swelling solvent. We measured the volumetric swelling ratio of IBC-105 coal
in PCE to be 1.03 at 25° and 1.06 at 90°C. The total sulfur content of the PCE
extract of IBC-105 is 2.1%, essentially the same as the ASTM organic sulfur
content of the feed coal. Sulfur contents of PCE extracts of weathered coals are
greater than that value by the amount of elemental sulfur extracted. In order to
characterize organosulfur compounds removed by PCE, several extracts were
fractionated on alumina(12) and on Pd impregnated silica gel.(13) Typical
recoveries of fractionated extracts for both PCE (non-polar) and THF (polar) are
shown in Table 3. Recovery data show that considerable polar material,
especially from the THF extract, remains bound to the column. Stripping the
column with pyridine followed by methanol did not raise the total recoveries
above 73% for PCE extracts or 40% for THF extracts. Elemental sulfur, when
present, elutes with the AHC fraction, in which it was detected by both HPLC and
GC/MS. Both fractionated and un-fractionated extracts were analyzed by Sulfur
Sensitive Gas Chromatography and Gas Chromatography/Mass Spectrometry at Argonne
National Laboratory. The results of that study are discussed in the following
paper.(10) The organosulfur compounds identified to date are typical of those

reported by others for non-polar extracts of bituminous coals.(13)(14)

CONCLUSIONS

PCE is an excellent solvent for the extraction of elemental sulfur from coals in that the process is quickly completed and very little organic material is lost from the feed coal to the solvent. However, only weathered coals contain elemental sulfur which is the result of pyrite oxidation. PCE extraction does not remove more than 10% true organic sulfur from most coals. Elemental sulfur dissolved in PCE reacts with coal at 120°C to become bound to the coal an effect which may explain why exhaustive extractions with other solvents have failed to yield elemental sulfur.

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Table 1

ASTM FORMS OF SULFUR AND S° EXTRACTED BY PCE FOR WEATHERED COALS

EIU #	Sample Bank #	% S° by PCE	% Total S	% Sulfatic ASTM	% Pyritic ASTM	% Org S (Diff)
HERRIN SEAM	ILLINOIS No. 6					
0930	APCSP-3	0.000	4.83	0.010	2.47	2.35
0630	IBC-105	0.0006	4.24	0.010	2.60	1.63
0620	IBC-105	0.037	4.46	0.373	2.26	1.83
0650	IBC-105	0.1085	4.31	0.77	1.45	2.17
E0935	APCSP-3	0.127	4.67	0.934	1.83	1.91
OTHER ILLINOIS/INDIANA COALS						
0300	IBC-101	0.034	4.23	0.127	1.40	2.70
0410	IBC-102	0.199	3.22	0.466	1.88	0.87
0710	IBC-107	0.032	3.77	0.272	0.71	2.79
RN20	INDREFUSE	1.54	11.7	5.96	4.46	1.28
0560	OHIO 5/6	0.058	3.44	0.381	1.18	1.83

ALL 10 SAMPLES: % S° = 0.260*[% Sulfatic S] - 0.028 r^2 = 0.993

HERRIN SEAM: % S° = 0.140*[% Sulfatic S] - 0.0048 r^2 = 0.994

Table 2

DECREASE OF ORGANIC SULFUR IN PRODUCT COALS AND TOTAL SULFUR MASS BALANCE

Sample Number	Wt% PCE Extract	Wt% Coal Product	Wt% Organic Sulfur in Product	% OS Lost	Mass Balance Sulfur
0410	1.57 %	97.5 %	0.88 %	1.34 %	93.3 %
0560	1.70	98.8	1.44	24.00	97.7
0620	1.77	99.8	1.70	7.28	91.2
0630	1.64	97.3	1.53	8.70	95.2

FRACTIONATION SCHEME

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                    SOLVENT EXTRACT
                          ‖ Alumina
                          ⇓
      ┌───────────────────┼───────────────────┐
      │           │               │            │
   HEXANE      BENZENE        CHLOROFORM     THF/EtOH
      │           │               │            │
      ↓           ↓               ↓            ↓
     AHC         PAC            N-PAC         HPAC

                   │ PdCl₂ / Silica Gel
                   ⇓
      ┌────────────┼────────────┐
      │            │            │
  Chloroform   Chloroform   Chloroform
   Hexane       Hexane      Ethyl Ether
      │            │            │
      ↓            ↓            ↓
     PAH         PASH         S-PAC
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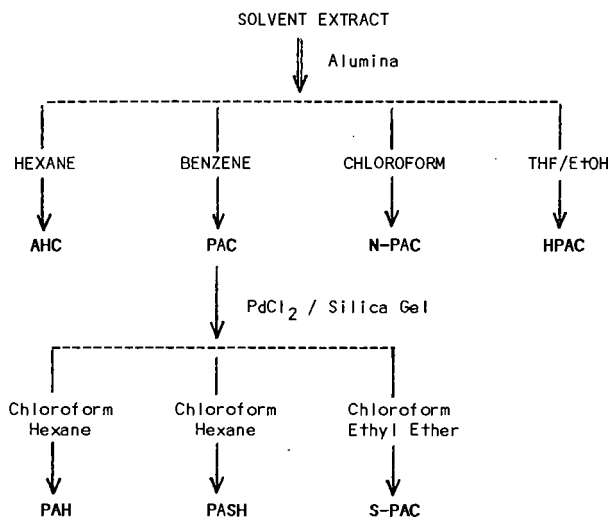
Table 3

FRACTIONATION OF PCE AND THF EXTRACTS

Sample Number	Extract Solvent	Wt % of Extract in Alumina Column Fractions			
		AHC	PAC	N-PAC	HPAH
0560	PCE	20.90 %	22.15 %	16.82 %	8.20 %
0630	PCE	7.24	14.79	15.73	21.54
0930	PCE	8.87	17.28	15.41	28.28
0630	THF	1.44	4.47	3.54	27.88
0930	THF	3.17	3.80	5.06	15.75

Sample Number	Extract Solvent	Wt % of PAC in Silica Gel Column Fractions		
		PAH	PASH	S-PAC
0630	THF	79.69	15.66	14.97

Wt % S Extracted vs Time

Effect of Temperature
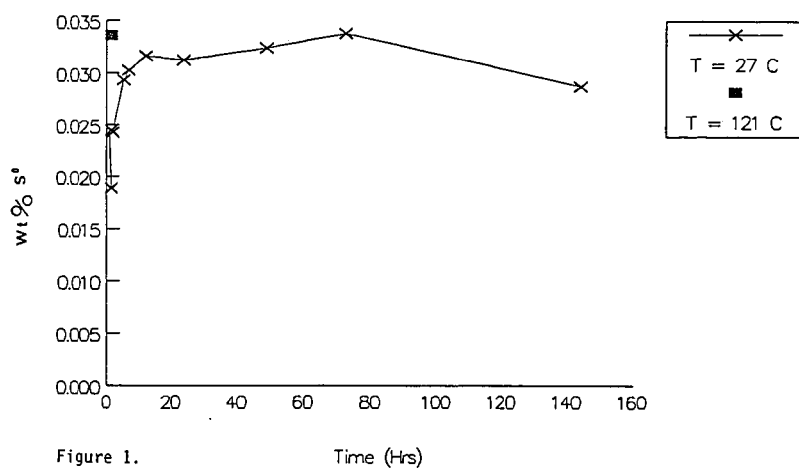

Figure 1.   Time (Hrs)

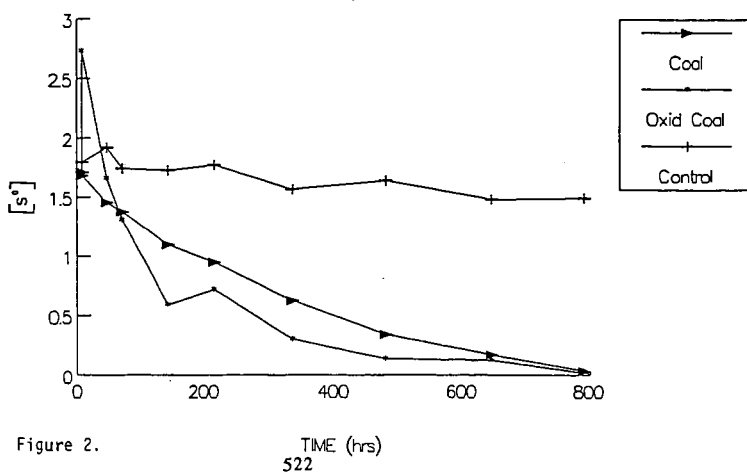## [Sulfur] in PCE vs Time

$T = 120°C$

Figure 2.   TIME (hrs)

Sulfur Species in Perchloroethylene and Other Coal Extracts

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INTRODUCTION

Earlier work (1,2,3) has indicated that elemental sulfur can be
removed from coal by the use of perchloroethylene
(tetrachloroethylene). The unique ability to remove the elemen-
tal form of the sulfur has led to considerable interest in te
process and mechanism of action. Under joint CRSC-EPRI sponsor-
ship, an effort has been made to understand the species that can
be removed by extraction with perchloroethylene (PCE). The ef-
fort involved the extraction of a set of coals at Eastern Il-
linois University by Prof. David Buchanan and coworkers, and the
related effort to identify the species in the extract by the use
of gas chromatography- mass spectrometry at the Argonne National
Laboratory (ANL). This paper reports on the analytical work on
the extracts.

EXPERIMENTAL

Extracts were prepared and sent in glass vials to ANL. The con-
tents of the vials were dissolved in solvents and studied in one
of two systems.

The first system was a gas chromatograph equipped with a Hall Ef-
fect Conductivity Detector (HECD). This detector was selected
because it can be made to be sensitive to sulfur-containing
species and will permit establishing the number of species in
very dilute concentrations. The HECD was mounted on a Tracor
Model 540 gas chromatograph, and attached to a strip chart re-
corder. A J&W DB-5 column (30 m, .25 mm id) was used. The typi-
cal run started at 85 C for 4 minutes and then the temperature
was increased at 10 C/minute to 320 C and held there for up to 30
minutes before cooling. The attenuator on the recorder was reset
as needed to keep the peaks on the chart. The settings were re-
corded on the chart. A series of standards was run to provide
retention time values for comparison with the observed peaks.

The HECD measures the conductivity of a sample which has been oxidized (in this case to SO_2) and introduced into a stream of purified methanol. This can be calibrated with standards of varying concentration to obtain quantitative data. The instrument is extremely sensitive to contamination from halogen containing-materials.

The system was calibrated for the amount of sulfur in the individual species by preparig different concentrations of thiophenol and making several runs to establish the response in terms of peak height per unit of mass of sulfur in the compound. The response was 5×10^{-12} grams of sulfur per one millivolt peak.

The second system was a Hewlett Packard GC/MS, model 5970B, which was set up using the same type of J&W DB-5 column used in the Tracor instrument. The same time-temperature profile used with the HECD system was employed to be able to compare the results on a common basis. At the beginning of each day the autotune procedure was used to assure that the instrument was performing to meet the manufacturer's specifications. A blank run was then carried out to check on performance of the chromatograph system and to check on the cleanliness of the solvent.

In a typical run, the chromatogram was displayed, data were saved, and analyzed later. The portion of the chromatogram to study was selected and the characteristics of the peaks to be included were specified. A macro was developed to analyze the mass spectral data for use with the Hewlett Packard computer system. Then for each peak the relative abundance for each mass was tabulated. The data were then checked against the library of about 133,000 spectra for the best matches. A graphical representation of the 4 best matches was printed together with a table of the 20 best matches. A numerical value of the "quality" of the match was included. A standard algorithm for this quality, developed earlier by McClafferty and coworkers, was used.

Initially the gas chromatograph was programmed to have a temperature increase of 10 C/minute for data acquisition. It became evident from the GC/MS results that a number of extracts contained many constituents. A precision temperature profile which used a 4 C/minute heating rate was then used to provide for better resolution of the peaks and improved identification of the species.

The coals used and samples derived from them included

Series 9391, 7107, 7111 and 7112
These extracts were prepared from Illinois #6 samples of the Argonne Premium Coal Sample Program (APCS) and the isotopically labelled sulfur sample of the Illinois Basin Coal Sample Program (IBCSP).
    APCS #3, pristine, PCE extract, EIU #9391
    IBCSP #7, oxidized, PCE extract, EIU #7107
    IBCSP #7, light organics from EIU 7107, EIU #7111
    IBCSP #7, heavy organics from EIU 7107, EIU #7112

Series 9395 and 9397
    These samples were prepared from APCS #3, a pristine starting material.
    Tetrahydrofuran extracts and fractionated on an alumina column to give the following EIU sample numbers
    EIU # 9395 AHC   Aliphatic hydrocarbons
    EIU # 9395 PAC   Neutral polycyclic aromatic hydrocarbons
    EIU # 9395 N-PAC Nitrogen polycyclic aromatic hydrocarbons
    EIU # 9395 HPAH Hydroxy polycyclic aromatic compounds
    EIU # 9395 Py   Pyridine eluent
    EIU # 9395 MeOH Methanol eluent

    Perchloroethylene extracts
    EIU # 9397 AHC
    EIU # 9397 PAC
    EIU # 9397 N-PAC
    EIU # 9397 HPAH
    EIU # 9397 Py

Series 6320
    These samples were prepared from IBCSP #5, unoxidized. These samples came from the same block of coal used for APCS #3.
    These samples were extracted with THF and fractionated on an alumina column to give the following EIU sample numbers:
    6320 AHC
    6320 PAC
    6320 N-PAC
    6320 HPAH
    6320 Py

The 6320 PAC fraction was further separated on a silica gel/PdCl2 column to give:
    6320 PAH
    6320 PASH
    6320 S-PAC, passed over a silica column.

Sample 6269

A PCE extract of oxidized IBCSP #5 was given the sample number 6269.

Sample 6201-38
    IBCSP #5, oxidized, PCE extract was sample number 6201-38.
    6201-38 untreated with NiCl2
    6201-38 treated with NiCl2

Sample 5618
    A THF extract of oxidized Ohio 5/6 coal is   5618. The sulfatic sulfur = 0.38%.

In addition to the extracts a number of standard compounds have been run in both instruments. For the HECD, this provided a set of retention times for checking the identity of compounds. For the GC/MS this provided a means of checking the mass spectra as well as retention times.

RESULTS AND DISCUSSION

    A number of species were found with the HECD in the extracts.   Retention times and peak heights were noted such that comparisons could be made later with GC/MS data.

Calibration data with thiophenol indicated that a peak of 1 mv was equivalent to an injection of one microliter containing 5 x 10^{-12} grams of sulfur. From this the percent of sulfur in the original extract due to these peaks has been calculated.

The data obtained with the HECD indicate that there are many sulfur species in the extracts. Peaks of retention times close to those for sulfur and dibenzothiophene have been observed. The number of sulfur species observed with this detector significantly exceeds the number that have been identified with the GC/MS. However the concentration of these species is so small, that their peaks are lost in the background of the GC/MS traces. The effort to quantify the peaks gave an indication of the amount of sulfur species that were present in the extracts examined with the HECD. The concentration of sulfur species identified in the extracts is usually such that they would account for at most 0.014% S in the sample extract. The organic sulfur content of the samples is at least 2 %.

The GC/MS work indicates that the peaks observed are typical of the aliphatic (n-alkanes) and aromatic (substituted naphthalenes) species present in coal samples. In addition a number of substituted thiophenes, benzothiophenes, dibenzothiophene, thiazoles, benzothiazoles and elemental sulfur have been observed

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in different samples. The most frequently observed and most abundant is dibenzothiophene. These data are consistent with the observations of Winans et al (10) on the existence of a number of heteroatom containing species in this sample.

In the HECD studies, the 9397 aliphatic hydrocarbon (AHC) extract contained two peaks close to those for sulfur in a total of 11 peaks. Elemental sulfur does elute with this fraction.

According to earlier reports elemental sulfur is not found in extracts of pristine coal samples (4). The results of this study are consistent with the earlier work. Elemental sulfur was seen in a PCE extract of an oxidized coal. This sample showed three forms of elemental sulfur differing in their molecular weights as the hexamer, heptamer and octamer. As expected the retention times increased with the molecular weight. Each comes off of the column at a reproducible retention time, and has a mass spectrum consistent with the particular polymer size. It is significant that the elemental sulfur is found in the oxidized sample which was later extracted with PCE, but not in the pristine samples.

The PCE does extract a series of species which on fractionation are typical of the fractions from better solvents. A range of n-alkanes was seen in the 9397 AHC fraction in addition to the tetramethyl longer chain hydrocarbons. The ability of PCE to remove some organic sulfur compounds from pristine samples is seen in the compounds identifed from 9397 PAC. These compounds included three different substituted benzothiophenes and diben-zothiophene. The nitrogen-containing polyclic fraction also had dibenzothiophene in it along with a possible isothiazole. The hydroxy polycyclic aromatic fraction had a small number of peaks, but they included substituted derivatives of benzenethiol, thiophene, benzothiazole and benzothiophene. In the latter case the quality of the matches were all low, but represent best choices from the available data.

The extracts which were analyzed without fractionation seemed to have too low a concentration of sulfur species for them to be ob-served. After fractionation, with the associated concentration of these species, the sulfur species were observed. The 9391 was a whole coal extract of pristine APCS #3 and showed almost no in-dication of a sulfur compound. The 9397 extract fractions showed evidence of sulfur compounds in three of the fractions (PAC, N-PAC and H-PAH). There were 10 peaks in the three fractions representing 9 compounds.

The THF fractions from the same pristine APCS #3 (9395 series) with sulfur compounds in them were essentially the same with the addition of the MeOH eluent. However there were fewer peaks observed (5) representing only 4 compounds. By comparison the PCE was more effective in solubilizing sulfur species. Only one was observed in both series (dibenzothiophene). The other compounds were different in the two series.

Those fractions with more sulfur species in the 9397 series were also observed to have more sulfur specie peaks in the HECD studies than the other fractions. The PAC fraction in 9397 had 4 compounds while the HECD showed 53 peaks, and the N-PAC fraction had two compounds while the HECD showed 12 peaks.

Some species were identified which are associated with solvents as preservatives (2-6 bis(1,1dimethylethyl)4 phenol and its oxidation product (1,1 dimethylethyl) 4 methoxy phenol. PCE extracts sometimes had hexachlorobutadiene in them as a product of reaction of two PCE molecules. Others are associated with pump oils such as 1,2 benzenedicarboxylic acid and its esters.

A number of isomers exist for some common compounds in these samples. A number of dimethyl naphthalene isomers were indicated. The difference in quality for these is too small to assign a retention time to a specific isomer. In several cases the compound has simply been listed as dimethyl naphthalene. Since these are not sulfur compounds, the specific identification of these species was not crucial to the study.

CONCLUSIONS

1.   Small quantities of a number of organic sulfur compounds are extracted from Illinois Basin coals by both perchloroethylene and THF. The amounts are much less than the total organic sulfur in the coal.

2.   Elemental sulfur is found in some of the extracts. These extracts are from oxidized coal samples.

3.   The elemental sulfur is found in the form of three oligomers with six, seven or eight atoms per molecule.

4.   The organic sulfur compounds identified include substituted thiophenes, benzothiophenes, dibenzothiophene, thiazoles, benzothiazoles and possibly others in concentrations lower than were detected with the GC/MS.

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5. The concentrations of sulfur species in whole coal extracts was too low to be observed with the GC/MS, but the concentration in the various chromatographic fractions did permit identification of sulfur species in some of the fractions.

6. The PCE extracted different sulfur compounds than the THF did, and extracted a larger number of them.

7. The fractions (PAC, N-PAC, HPAH) which contained sulfur compounds from PCE extractions also contained these types of compounds in the THF extractions.

8. The PCE and THF extracts contained a range of aliphatic and aromatic compounds common to Illinois #6 coal.

ACKNOWLEDGMENTS

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ANION EFFECTS ON CALCIUM CATALYSIS OF LOW-RANK COAL CHAR-STEAM GASIFICATION·

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ABSTRACT

Limestone (primarily $CaCO_3$) has been shown to be an excellent bed material in a fluidized-bed reactor operated at 700-800°C and atmospheric pressure for the steam gasification of coal. It not only maintains its physical integrity under these conditions but also has shown catalytic effects on a subbituminous coal-steam reaction that are comparable with the effects of an alkali salt. The study reported in this paper concerns the effect, if any, of calcium-associated anions on the reaction kinetics of the coal char-steam reaction. Velva lignite and Wyodak subbituminous coals to which CaO, $CaSO_4$, limestone, or $Ca(C_2H_3O_2)_2$ had been added, were charred in a thermogravimetric analysis unit (TGA) and then were immediately reacted with steam at the temperature and pressure conditions described above. Both coals showed less catalytic effect for limestone and calcium sulfate than for the other two additives. The rate for the Wyodak char-steam reaction increased steadily over 700-800°C with calcium oxide whereas the Velva rate increased rapidly to the maximum between 700-750°C. Apparent activation energies along with surface analyses of selected samples to determine catalyst dispersion and form will be presented.

INTRODUCTION

Gasification of coal has been shown by many researchers to be greatly enhanced by the addition of alkali or alkaline-earth compounds to the reaction mixture. In the case of the alkali compounds, the excellent catalytic effect of carbonates, hydroxides and bicarbonates, and the somewhat lesser effect of chlorides and sulfates of potassium and sodium are well documented. However, the reasons for the large differences in catalysis that occur with changes in anion have not been satisfactorily explained, and those reasons have been the focus of only limited study, since the negative aspects of using potassium and sodium minerals as catalysts make them impractical to use under present processing conditions. The major drawback to using potassium is the relatively high cost of its catalytically active minerals. Although sodium compounds are plentiful in mineral deposits (trona, nahcolite, sodium chloride) and therefore relatively inexpensive, the inherent problems, such as fouling and agglomeration, associated with having sodium in a reactor make them unsatisfactory additives. Limestone, largely calcium carbonate, has been shown to have a catalytic effect on the reaction between low-rank coal char and steam at temperatures of 700-800°C and ambient pressure in a continuous process unit (CPU)(1). This mineral is not only inexpensive and causes few reactor problems, but also is, in fact, a viable candidate for bed material in fluidized-bed reactors and is promoted by some researchers as an in-bed sulfur-capture material. The question as to the importance of the carbonate, if any, on the activity of the catalyst was addressed in this study by substituting other calcium compounds for limestone in two previous thoroughly-studied char-steam reactions. The answer to the question was expected to provide some understanding of the effect of the anion on the reactivity of the char-steam reaction.

Table 1 shows the elemental analyses of the ash of the raw coals. Both of the coals reacted had a high calcium content.

EXPERIMENTAL

Laboratory reactivity testing was carried out at 700, 750, and 800°C and ambient pressure on a DuPont 951 Thermogravimetric Analysis (TGA) module interfaced with a DuPont 1090 Thermoanalyzer data station. Approximately 40 milligrams of -60 x 0 mesh raw coal containing 10 wt% catalyst was devolatilized in vitro, followed immediately by reaction of char carbon with steam as previously reported (2). The reactivity parameter, k, was calculated for 50% carbon gasification in each test.

Pilot-scale data was obtained from experiments carried out in a nominal 30-lb/hour CPU operating at ambient pressure and temperatures similar to those reported for the TGA experiments (1).

CALCIUM CATALYST SCREENING

Wyodak subbituminous and Velva lignite char-steam reactions were carried out using four calcium-containing catalysts, calcium oxide, calcium sulfate, limestone, and calcium acetate, at 700, 750, and 800°C and atmospheric pressure. The choice of limestone is obvious (see Introduction). Calcium oxide was chosen because it has been reported to be the predominant species responsible for catalysis of the gasification reaction (3). Calcium acetate was selected since it is water soluble and, upon heating, decomposes into calcium carbonate and acetone. Since calcium sulfate is insoluble and does not readily decompose at the temperatures of this study it was the final choice. The Arrhenius energy of activation, Ea, and the correlation coefficient, r2, for the Arrhenius plot, along with the reactivity parameter of each of the reactions is reported in Tables 2 and 3. In addition, k values calculated from CPU data are also given for experiments where limestone was used as bed material. There appears to be a significant difference in the catalysis of the Wyodak char-steam reaction among the materials tested.

TABLE 1

XRFA RESULTS OF ASH PREPARED FROM AS-RECEIVED VELVA LIGNITE
AND WYODAK SUBBITUMINOUS COALS USED IN HYDROGEN PRODUCTION TESTS

Element	Velva Ash % Elemental	Wyodak Ash % Elemental
Silicon	5.57	11.44
Aluminum	5.00	7.55
Iron	12.73	12.45
Titanium	0.38	0.76
Phosphorous	0.20	0.55
Calcium	25.49	14.80
Magnesium	6.52	3.53
Sodium	0.45	0.92
Potassium	0.00	0.00
Sulfur	4.68	5.47
Oxygen (Diff.)	38.98	42.53
Ash	6.94	9.05

TABLE 2

REACTIVITY PARAMETER FOR WYODAK CHAR-STEAM REACTIONS CATALYZED
WITH VARIOUS CALCIUM-CONTAINING SUBSTANCES.

TEMP, C°	Uncat.	Limestone k, in g/hr/g		CaO	CaSO$_4$	Ca(Ac)$_2$
		TGA	CPU			
700	1.33	1.26	1.60	3.80		
750	3.28	3.01	3.53	6.36	2.77	4.33
800	7.33	3.86	38.98	15.74		
E$_a$	35.45	23.35	65.64	29.34		
r^2	1.00	0.92	0.95	0.97		

TABLE 3

AVERAGE REACTIVITY PARAMETER FOR VELVA CHAR-STEAM REACTIONS
CATALYZED WITH VARIOUS CALCIUM-CONTAINING SUBSTANCES.

TEMP, °C	Uncat.	Limestone k, in g/hr/g		CaO	CaSO$_4$	Ca(Ac)$_2$
		TGA	CPU			
700	2.40	4.95	2.24	6.89		
750	4.95	6.84	5.45	8.01	4.75	6.80
800	6.89	6.95	49.13	10.86		
E$_a$	22.05	7.14	63.57	9.38		
r^2	0.97	0.81	0.96	0.95		

RESULTS AND DISCUSSION

Dispersion of catalyst over the organic matrix is a major consideration when studying gasification and catalyst effects (4,5).

Each of the catalysts studied was applied by admixing 10 wt% with coal. Impregnation was not used so as to preserve the integrity of the anion on contact with the raw coal. Of the four calcium catalysts chosen, two (acetate and oxide) were soluble in water and two were not. In coal with 30+% moisture, water-soluble catalyst can disperse into water-filled micropores as well as over the moist surface of particles. In addition, the CaO forms a base, Ca(OH)$_2$, when dissolved in water enabling it to better penetrate the coal structure. However, since the water-insoluble catalysts (carbonate and sulfate) were applied as <150 um particles, they were limited to a finite number of contact surfaces and were probably excluded from most micropores. The variation in solubility that results in differences in catalyst dispersion accounted for some of the effects noted in the study.

The uncatalyzed char-steam reactions had rate constants, k, which were slightly higher at 700°C and 750°C for Velva than for the Wyodak char. This was attributed to catalysis caused by the higher inherent calcium content of the Velva coal. The Velva coal has 33% more calcium and magnesium than the Wyodak coal on a mole-of-element/gram-of-coal basis. The inherent sodium content of the Wyodak, albeit small, was more than twice as great as that of the Velva but probably too small to give obvious rate increases. Silicon and aluminum, which are known catalyst killers, were nearly three times and two times as abundant, respectively, in Wyodak as they were in Velva. However, at 800°C the Wyodak k was slightly higher than that of the Velva, probably because of limitations due to physical effects such as mass transport rather than chemical reactivity (6).

The catalyst effects observed in this study varied between the two coals. The CaO gave reactivities which were similar for the two coals at 700°C and 750°C but was 1.5 times greater for the Wyodak than for the Velva at 800°C. The limestone-catalyzed reactions had reactivities that were two-fold greater for the Velva than for the Wyodak at each temperature. The calcium acetate-catalyzed Velva char-steam reactivity at 750°C was ⁻1.5 times larger than that of Wyodak. The calcium sulfate appeared to have no positive catalytic effect at 750°C with either coal char.

The catalytic effect of the calcium on the char-steam reaction for each coal varied substantially with the associated anion. With the Wyodak coal little positive effect was observed for the limestone at the three temperatures tested, and no positive effect, and perhaps even some inhibition, was observed for the calcium sulfate at 750°C. The calcium oxide doubled the reactivity of the Wyodak, but it must be realized that a 10 wt% loading of this material provides 7 wt% calcium whereas the other catalysts tested contributed <4 wt% of the element. Calcium acetate also increased the reactivity of the Wyodak at 750°C even though 10 wt% provides only 2.8 wt% calcium.

With the Velva coal, limestone exhibited catalysis at the lower two temperatures. Calcium oxide, as with the Wyodak coal, enhanced the reaction at all three temperatures. At 750°C calcium sulfate did not catalyze the reaction but the acetate conferred as much catalysis as the limestone at the same temperature.

The Arrhenius energy of activation, Ea, varied greatly with calcium catalyst in this suite of tests. Wyodak, even in the presence of additive, had a much higher energy requirement for reaction than the Velva.

A comparison of the rate constants obtained using limestone catalyst on the TGA with those of the Continuous-Process-Unit (CPU) showed good agreement at 700°C and 750°C but lack of agreement at 800°C. The fluidized bed provided for improved heat transfer and mass transport compared to the fixed bed of the laboratory unit. In addition, the temperature of the reported 800°C experiment in the CPU was actually 10 to 15 degrees hotter than that of the bench-scale experiments. The limestone used in this experiment undergoes a thermally induced transition at 800°C as shown by Differential Thermal Analysis (DTA) resulting in what appeared by Scanning Electron Microscope (SEM) to be fragmentation of the limestone particles and the subsequent wider dispersion of catalyst. Thus the difference in rate constants for the two reactors at 800°C was probably due to a relatively large TGA sample size which resulted in transport limitations and the lower TGA reaction temperature. The deviation of the correlation coefficient (r2) from 1.00 could also be an indication of those limitations, although from this study there is no basis for ruling out a change in mechanism.

CONCLUSIONS

- Calcium catalysis of char-steam reactions of low-rank coals is affected by the associated anion.

- Rate constants determined by TGA are comparable with those obtained with the 30-lb/hr CPU.

- Water-soluble calcium compounds are better low-rank coal reaction promoters than those that are insoluble.

- Calcium inherent to the coal does not necessarily affect catalysis by calcium additives.

ACKNOWLEDGEMENTS

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Characterization of Syncrude Sludge Pond Tailings*

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The hot water process used by Suncor and Syncrude to extract bitumen from the Athabasca Oil Sands produces large volumes of tailings slurry. The fine grained sludge component of this waste is the most troublesome because of its stability and poor compaction potential. The sludge apparently owes its stability substantially to a complex interaction between organic coated amorphous particles, clays and bitumen. In this study we have investigated the nature of both the minerals and the associated organic matter present in a thickened, aqueous tailings sludge sample, from the Syncrude Canada Limited plant. An oil phase agglomeration technique was used to remove free bitumen and associated oil wettable solids from the sludge. On standing, the treated sludge, unlike a comparable blank, separated into settling and non-settling fractions. The solids from these fractions were analyzed by; X-ray diffractometry, Inductively Coupled Plasma Atomic Emission Spectrometry, Solid State MAS ^{29}Si and ^{27}Al NMR spectroscopy in an attempt to characterize the inorganic minerals present. The oil phase solids showed considerable enrichment in heavy metals compared to the other solids. The findings of this study could be helpful in providing some insight into the nature of tailings pond sludge, a problem which poses the most imminent environmental constraint to future use of the "hot water" process.

INTRODUCTION

Two commercial oil sand extraction plants in Alberta generate vast quantities of tailings slurry as a result of the hot water extraction of bitumen from tar sands.[1-3] The fine-grained sludge component of this waste is the most troublesome because of its stability and poor compaction potential. The reason for the intractability of the sludge has been the subject of considerable study.[1,3-7] Based on some recent studies, it is generally believed that toluene insoluble organic matter (IOM) associated with certain

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largely amorphous solids could be partly responsible for the stability and incompressibility of the oil sand slimes.[2,5-7] It is believed that the IOM causes particle surfaces to develop some hydrophobic character, allowing particle bridging, possibly through the medium of residual bitumen, thereby setting up a gel structure.[7,8] Another reason for the stability of oil sands sludge is said to be the presence of fine clay platelets which, with their differential edge and force-wetting properties, can also assist in the stabilization of suspensions[2,9].

In our previous work, we have isolated and characterized insoluble organic matter from a number of oil sand tailings streams obtained from both the Suncor and Syncrude plants.[6,7] More recently we have fractionated sludge from the main Syncrude Canada Ltd. tailings pond. After removal of the emulsified bitumen by an oil phase agglomeration technique the sludge solids separated into settling and non-settling fractions. The insoluble organic matter associated with the fines present in the non-settling portion of the sludge was concentrated by an acid dissolution scheme[6] and then characterized using elemental analysis and solid state ^{13}C NMR spectroscopy[10]. In this communication we, report the analysis of inorganic mineral fractions using X-ray diffractometry, Inductively Coupled Plasma Atomic Emission Spectrometry, and ^{29}Si and ^{27}Al NMR Spectroscopy.

EXPERIMENTAL METHODS

Sample

Aqueous sludge from the 17 m level of the Syncrude tailings pond[11,12] was provided to us by Drs. R. Schutte and L. Danielson of Syncrude Canada Ltd. in 4-litre jugs. Prior to further sub-sampling, the samples were thoroughly mixed by vigorous manual agitation.

Oil Phase Agglomeration Treatment

A countra-rotating stirring device (grease kettle) was used to remove bitumen from the sludge[10,13] using vacuum still bottoms as the oil collection phase. After removal of bitumen the aqueous sludge was fractionated as shown in Figure 1. The aqueous phase was transferred into a 500 mL beaker and the contents allowed to gravity settle for one week. The suspension was then decanted off to leave the settled solids. Water was evaporated at 100°C to obtain the solids from the supernatant liquor. The dried solids fraction from the suspension was deminieralized using HCl and HF in order to concentrate the organic matter associated with the mineral fines[6].

NMR Measurements

^{29}Si MAS NMR spectra (spinning rate ≈3.5kHz) were recorded at 59.60 MHz on a Bruker MSL-300 NMR spectrometer (magnetic field 7.1 T). About 4,000 free-induction decays (FIDs) were accumulated at a repetition time of 2s. Chemical shifts are given in ppm with respect to tetramethylsilane (TMS).

^{27}Al MAS NMR spectra were recorded at 78.172 MHz on the same instrument using a repetition time of 1s. The number of free-induction decays accumulated were 6 for solids VI and 145 for the other two samples. ^{27}Al chemical shifts were measured with respect to solid $Al(H_2O)_6^{3+}$.

Mineral Composition. Mineral (crystalline) composition of the samples was determined semi-quantitatively by comparing their X-ray diffraction (XRD) peak intensities with those of standards. XRD patterns were recorded using a SCINTAG PAD V automated powder diffractometer equipped with a graphite monochromator, using CoKα radiation (λ= 1.7902Å). The amount of each of the minerals in the samples was estimated by multiplying the peak intensity of the characteristic reflection for the respective mineral by the intensity factor for that mineral, determined from XRD data for a set of standard mixtures. The standards were measured under identical experimental conditions, including sample preparation radiation source and diffraction geometry. The amount of poorly-crystalline components (X-ray amorphous) was expressed by the difference of 100 and the total % of crystalline components.

Heavy Metal Analysis. Quantitative Industively Coupled Plasma Atomic Emission Spectroscopic methods (ICP-AES) were used to analyze the ash for Ti, Zr, Cu, Ni, Cr, Mn, Al, Ca, Fe and Mg.

RESULTS AND DISCUSSION

The separated solids fractions were treated according to the scheme shown in Figure 2. The non-settling portion was leached with HCl and HF in order to concentrate the insoluble organic matter associated with this fraction. Table I lists the semi-quantitative X-ray diffraction analysis of the mineral matter fractions shown in Figures 1 and 2. The following conclusions are obvious from examination of the data in Table I.

1. The proportion of amorphous material was higher in the suspended solids than in the sediment.

2. Solids obtained from the washing of the oil phase had the lowest quantity of amorphous material and the highest quartz content of all the solids fractions.

3. The proportion of mica and kaolinite clays in the sediment was higher than in the non-settling solids.

4. There is an unexpected discrepancy in the determination of amorphous material in the ashed and unashed samples of solids II and III.

These results suggest that removal of bitumen has a marked effect on the structure of sludge, freeing the bulk of the crystalline minerals and allowing them to freely settle out. Also, the remaining suspended solids, associated with larger amounts of amorphous material and insoluble organic carbon (IOC), were found to settle more readily, although slowly, from the treated sludge than from the untreated sludge. This suggests that bitumen present in the sludge interacts with some component of the sludge solids to form a structure which is capable of entrapping particles that would otherwise settle.

Table II lists the elemental analyses of ashed solids obtained from the fractionation of Syncrude sludge. Solids III obtained by washing the oil phase, after sludge treatment, contained the lowest concentrations of heavy metals which is consistent with the very high quartz content found in these solids. Solids IV (suspension solids) had higher concentrations of Al, Mg and Zr but lower concentrations of Cr and Mn than solids II from the sediment. Concentrations of Ti, Fe and Ca in the two fractions was similar. Whereas solids IV from the suspension comprise a large proportion of both the X-ray amorphous material and the elements Al, Mg and Zr it seems likely that these components are directly associated.

Leaching of the suspension solids IV with dilute HCl dissolved the Ca and Mn almost quantitatively plus the greater part of the Fe, Al, Mg and Cr. However, Ti and Zr appeared to resist dissolution by HCl as seen from the enrichment of these elements in the HCl extracted solids V.

Treatment of solids V by HF produced a solution with Al as the major element followed by Fe, Ti and Zr. Minor constituents in the HF solubles included Mg, Ca, Cr and Mn.

Table III lists the elemental distribution among solids fractions VI to VIII. It is obvious from this data that the bulk of the Ti and Zr has been unaffected by treatment with HCl and HF with over 60% of these elements being insoluble. Thus it seems likely that Ti and Zr are strongly complexed with the IOM and that these complexes are not readily decomposed by the acid treatment.

Almost quantitative dissolution of Ca and Mn in HCl was achieved, suggesting that these elements are not complexed to IOM but are present as inorganic minerals. Al, Fe, Mg and Cr exhibit an intermediate solubility, indicating that they could be present as a mixture of free inorganic minerals and as complexes with the IOM.

Solid State ^{29}Si and ^{27}Al MAS NMR

The ^{29}Si MAS NMR spectrum of non-settling solids from suspension (Figure 3a) shows a sharp resonance at 92 ppm from TMS with a very weak shoulder around -88 ppm. These features fall in the ^{29}Si chemical shift range of layer structured phyllosilicate (Q^3) minerals[14]. Examples of these minerals include trioctahedral silicates like serpentine and dioctahedral aluminosilicates like pyrophyllite and kaolinite.

The ^{27}Al MAS NMR spectra of dried sludge and suspension solids from clean sludge are shown in Figures 3b and 3c respectively. Both spectra consist of a single peak at -4 ppm with respect to $[Al (H_2O)^6]^{3+}$ as an external reference. This suggests that Al in these samples is exclusively in octahedral coordination.

On treatment of suspension solids with 6M-HCl $\approx$ 30% of the material leached out. Infrared and DC-Arc spectrographic analysis of this material was consistent with $AlCl_3 xH_2O$ being the major component and Zn, Fe species as trace amounts. Figure 3d is the ^{27}Al MAS NMR spectrum of this material. The spectrum consists of a single sharp peak at -1 ppm indicating the presence of octahedral Al alone.

CONCLUSIONS

1. The suspension solids separated after oil phase agglomeration of Syncrude sludge contained a higher proportion of X-ray amorphous material than the settled solids. The suspension solids also had a higher concentration of Al, Mg and Zr suggesting that these elements were associated with the amorphous solids.

2. The resistance of Ti and Zr towards dissolution by HCl and HF suggests that these metals could be complexed with insolube organic matter (IOM).

3. Al, Fe and Cr appear to be present as a mixture of soluble inorganic minerals and as insoluble complexes with IOM.

4. Solid state ^{29}Si NMR spectrum of the suspension solids suggested the presence of phyllosilicate minerals, conforming to the minor amounts of kaolinite detected by X-ray diffractometry.

5. Solid state ^{27}Al NMR spectra indicated that Al in these samples was exclusively in the octahedral coordination.

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Table I   Semi-quantitative X-ray Diffraction Analysis of Mineral Matter
Fractions from Syncrude Sludge Pond Tailings*

Fraction No.†	Description		Mica	Kaolinite	Quartz	X-ray Amorphous
			Concentration Range (wt. %)			
—	Dried Untreated Sludge					
		Un-ashed	10-25	10-25	10-25	40
		Ashed	10-25	10-25	10-25	40
1	Sediment from Untreated Sludge					
		Un-ashed	10-25	10-25	25-40	25-40
2	Sediment from Clean Sludge					
		Un-ashed	10-25	10-25	25-40	25-40
		Ashed	10-25	25-40	25-40	1-10
3	Washings from Recovered Bitumen					
		Un-ashed	1-10	1-10	40	10-25
		Ashed	10-25	1-10	40	1-10
4	Suspension Solids from Clean Sludge					
		Un-ashed	1-10	1-10	1-10	>40
		Ashed	1-10	1-10	1-10	>40
5	HCl Treated Suspension Solids from Clean Sludge					
		Un-ashed	1-10	1-10	1-10	>40
		Ashed	1-10	1-10	1-10	>40

* In addition to the amount of major minerals listed in the table, small amounts of the following
minerals were also detected in some of these fractions:
Interstratified Minerals minor amounts (1~10%) in Fractions 1,2 and dried sludge;
Microcline , trace (<1%) in Fraction 1; Plagioclase, trace (<1%) in dried sludge;
Lepidocrocite minor quantities in dried sludge, and Siderite in minor quanitites in Fraction 2
† According to Figure 1 and 2

Table II   The Elemental Composition of the Mineral Portion of Various
Fractions from Syncrude Sludge Pond Tailings (Figures 1 and 2)

Fraction No.†	Yield (g/100 g sludge)	Ash (wt %)	C (wt%)	Elemental Analysis (wt. % of ash)*							
				Ti	Fe	Al	Ca	Mg	Zr‡	Cr‡	Mn‡
1	2.0	94.2	3.7	0.5	2.2	8.8	0.18	0.41	180	88	620
2	11.5	94.3	3.7	0.56	2.9	10.3	0.25	0.41	130	220	950
3	1.6	83.3	3.0	0.40	0.5	3.5	0.02	0.12	100	33	52
4	13.0	92.4	5.8	0.50	2.4	12.5	0.25	0.72	230	120	410
5	9.0	88.9	7.9	0.73	1.4	7.3	0.011	0.22	330	67	21
6	2.2	100**	1.9	2.05	3.6	16.3	0.06	0.1	930	190	53
OPS	0.1	70	17.3	1.7	10.5	7.4	N.D.	N.D.	660	7200	N.D.

†   Figures 1 and 2
‡   as ppm
N.D. not determined
*   Cu and Ni in all fractions other than OPS were below the detection limit of the instrument.
    Concentration in OPS: Ni - 0.23%; Cu - 490 ppm; V - 190 ppm
** Analyzed as un-ashed samples

Table III   Elemental Distribution by Repeated Acid Leaching of Non-settling Solids from Syncrude Sludge

Fraction	Elemental Distribution (wt. % of amount in solids IV)*							
	Ti	Fe	Al	Ca	Mg	Zr	Cr	Mn
Solids VI; HCl Solubles	2.8	61.1	61.1	97.1	79.6	4.4	62.8	96.6
Solids VIII, HF Solubles	75.10	27.5	23.9	4.4	2.5	74.1	29.0	2.4
Solids VII**	22.1	11.5	15	-	17.9	21.5	8.2	1.0

· HCl Solubles = $\frac{y-x}{y} \times 100$ where y = Elemental amounts in solids IV calculated as:
Elemental concentrations from Table II x 0.13 (yield fraction) x 0.924 (ash fraction)
X = Elemental amounts in solid V calculated as:
Elemental concentrations from Table II x 0.09 (yield fraction) x 0.889 (ash fraction)
HF Solubles = $\frac{z}{y} \times 100$ where z = Elemental considerations from Table II x 0.022 (yield fraction)
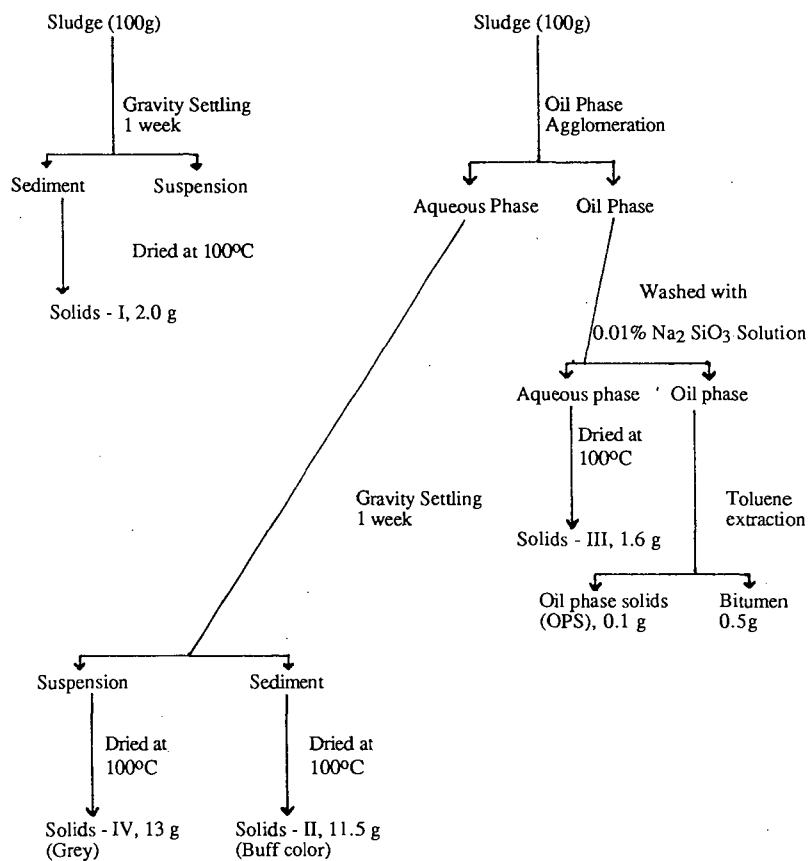
·· calculated by difference

Sludge (100g)

Gravity Settling
1 week

Sediment   Suspension

Dried at 100°C

Solids - I, 2.0 g

Sludge (100g)

Oil Phase
Agglomeration

Aqueous Phase   Oil Phase

Washed with

0.01% Na$_2$ SiO$_3$ Solution

Aqueous phase   Oil phase

Dried at
100°C

Gravity Settling
1 week

Solids - III, 1.6 g

Toluene
extraction

Oil phase solids   Bitumen
(OPS), 0.1 g   0.5g

Suspension   Sediment

Dried at   Dried at
100°C   100°C

Solids - IV, 13 g   Solids - II, 11.5 g
(Grey)   (Buff color)

Figure 1. Fractionation scheme for Syncrude Sludge Pond Tailings.

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Solids - IV, 10 g

Leached by 6 M. HCl,
60°C, 48 hrs.

Solubles
Solids - VI, 2.3g
(yellow)

Insolubles
Solids - V, 6.9 g
(grey)

48% HF, 50°C
Dryness

Insolubles
Solids - VII, 0.54 g (black)
(Organic Concentrate)

Solubles
Solids - VIII, 1.7 g
(white)

Extraction with Toluene

Bitumen, 0.27 g

Humic matter, 0.25 g

Extraction with
0.5 M. NaOH

Humic acid
0.05 g

Humin
0.2 g
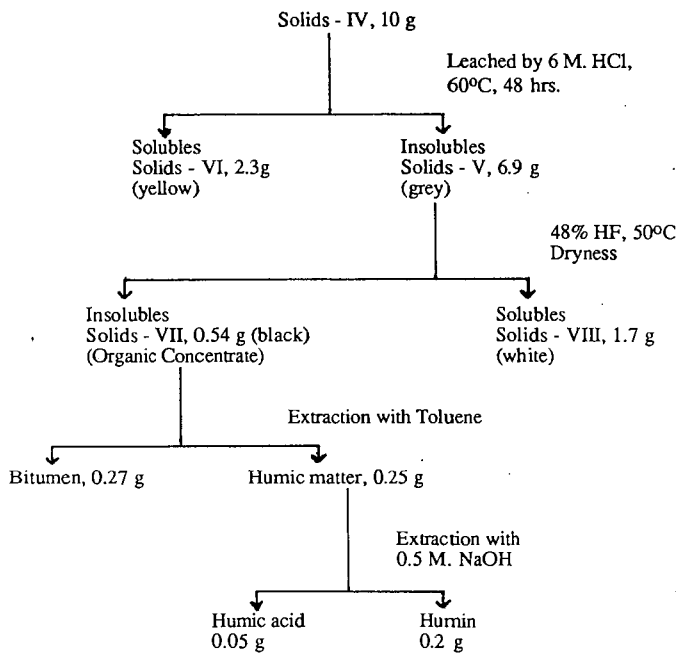
Figure 2. Flow sheet for the treatment of non-settling solids by
successive acid leaching and extraction of humic acids
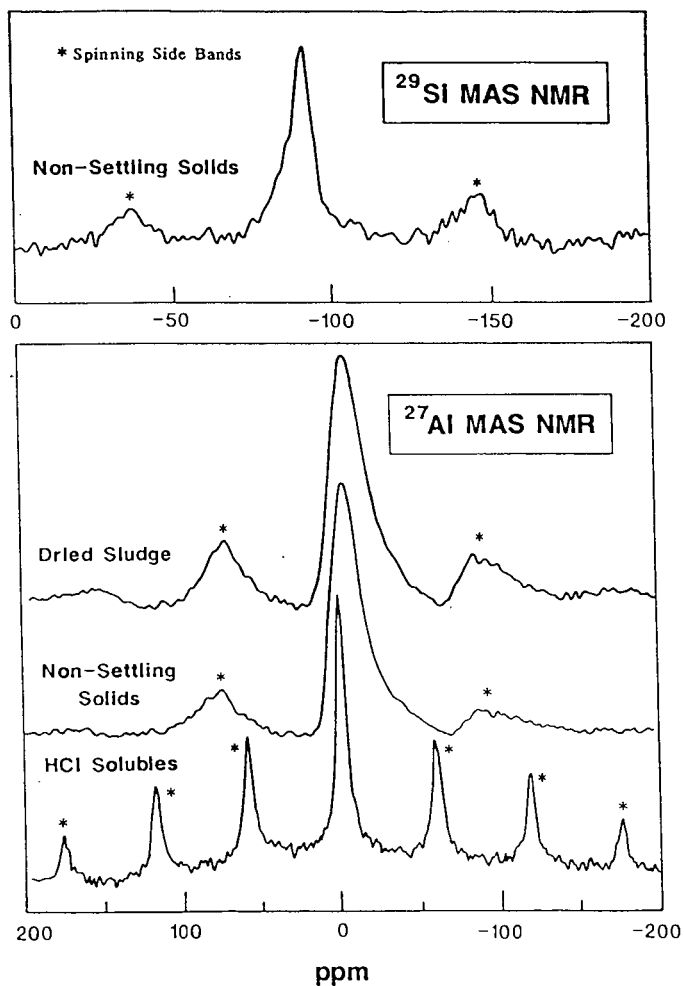
Figure 3a) ^{29}Si MAS NMR spectrum of suspension solids.

b-d) ^{27}Al MAS NMR spectra of b) dried Syncrude Sludge, c) suspension solids from clean sludge and d) HCl solubles from suspension solids.